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Investigation of the nature of the unpaired electron states in the organic semiconductor N-methyl-N-ethylmorpholinium-tetracyanoquinodimethane

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The nature of the unpaired electron states in the dimerized phase of the crystalline organic semiconductor N-methyl-N-ethylmorpholinium-tetracyanoquinodimethane [MEM(TCNQ)₂] is investigated by the combined means of polarized-optical-reflectance measurements and microscopic theoretical analysis. It is found that each unpaired electron is localized on a dimeric TCNQ unit, and it is demonstrated that the two-site molecular orbital (MO) which accommodates the unpaired electron involves internal molecular distortion of the dimeric unit. Experimental values are deduced for the intradimer π MO hopping integral, the TCNQ monomer a_g molecular-vibration frequencies and linear-electron-molecular-vibration coupling constants, and the difference in energy of the slightly nonequivalent TCNQ monomer π MO's. The dimer charge oscillation associated with the extremely weak coupling of the unpaired electron to the high-frequency a_g C-H stretch mode of the TCNQ molecule is observed for the first time.

I. INTRODUCTION AND SYNOPSIS

Recently, the Gröningen group¹⁻⁴ has investigated the physical properties of the intermediate conductivity complex TCNQ salt N-methyl-N-ethylmorpholinium-tetracyanoquinodimethane MEM(TCNQ)₂. In common with all the compounds which belong to this interesting class of TCNQ salts the planar TCNQ molecules in MEM(TCNQ)₂ stack to form linear conducting chains.⁵ Since MEM is present as a closed-shell cation in this salt, the chemical formula MEM(TCNQ)₂ indicates the formal presence of one-half of an unpaired electron on each TCNQ molecule. These electrons are accommodated by the b_{2g} π molecular orbital (MO) of the TCNQ molecule⁶ and are responsible for the origin of electrical conductivity. Between 20 and 335 K, MEM(TCNQ)₂ exists in a triclinic crystalline phase in which the linear TCNQ chains are strongly dimerized with alternating interplanar distances of 3.15 and 3.27 Å.² The mode of the intradimer overlap is quite different from that of the interdimer overlap. These modes of overlap are illustrated in Figs. 1(a) and 1(b), respectively. The former favors a strong interaction of the π MO's while the latter is indicative of a weak interaction of orbitals. These considerations point to a ground state in which the unpaired electrons singly occupy one-electron states which are predominantly localized on the dimers and weakly interacting with each other.

Single occupancy, in the ground state, would be dictated by the Coulomb repulsion between the unpaired electrons. The magnitude and temperature (T) dependence of the observed paramagnetism is consistent with a linear array of localized unpaired spins subject to weak nearest-neighbor antiferromagnetic exchange coupling.^{1,3} The magnitude of the activation energy,⁴ $\Delta_0 \approx 0.4$ eV for electrical conductivity σ in the direction of the chain axis (crystal c direction), is not inconsistent with the thermal promotion of mobile defect pairs, consisting of doubly occupied and unoccupied localized states. At room temperature $\sigma \approx 10^{-2} (\Omega \text{ cm})^{-1}$.

At approximately $T = 335$ K MEM(TCNQ)₂ undergoes a transition to a new structural phase in which the TCNQ molecules are stacked almost uniformly.⁴ The dc conductivity jumps discontinuously to about $30 (\Omega \text{ cm})^{-1}$, and in the new phase is only weakly T dependent. At low temperatures there is yet a third structural phase.⁴ In the region of $T = 20$ K the unit cell of the dimerized phase doubles, leading to a tetramerized linear chain structure and loss of spin paramagnetism. The Gröningen workers have ascribed this transition to a spin-Peierls transition,^{3,4} involving alternation in the interdimer spacing which, we note, is similar to that occurring in the complex salt triethylammonium (TEA)(TCNQ)₂ at room temperature.

The purpose of the present paper is to investi-

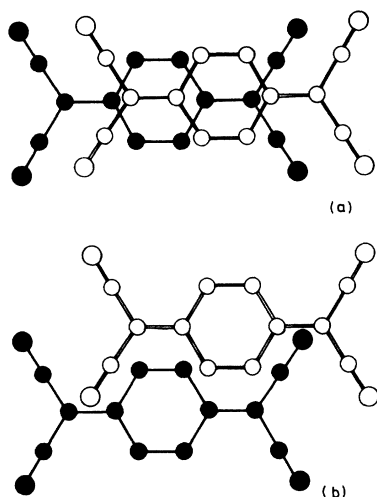


FIG. 1. Modes of TCNQ overlap in $\text{MEM}(\text{TCNQ})_2$; (a) intradimer overlap, (b) interdimer overlap.

gate the nature of the unpaired electron states in the dimerized phase of $\text{MEM}(\text{TCNQ})_2$. If each unpaired electron is localized on a dimeric TCNQ unit, the spectrum of low-lying excitations of $\text{MEM}(\text{TCNQ})_2$ should be that of a radical-ion TCNQ dimer. A detailed theoretical description of this spectrum has been given recently by one of the present authors.⁷ It consists of a primary electronic charge-transfer (CT) mode and a series of oscillations in the radical electron-electric dipole moment driven by the antisymmetric modes of internal molecular vibration of the dimer. The latter are a consequence⁸ of the intramonomer electron-molecular-vibration (EMV) coupling and, for short, we shall refer to them as "dimer charge oscillations." The spectrum may be directly verified by means of polarized-optical-reflectance measurements. We report in this paper the results of such measurements taken on large single crystals of $\text{MEM}(\text{TCNQ})_2$ at room temperature and in the optical range 50–30 000 cm^{-1} .

For application to $\text{MEM}(\text{TCNQ})_2$, the existing theory⁷ of the dimeric excitation spectrum requires a minor but interesting modification to allow for the slight inequivalence of the TCNQ monomers which constitute the dimeric unit in this compound. The inequivalence of the monomers is indicated by the observation² of slightly differing internal bond lengths and is a consequence of an asymmetric neighboring cation arrangement in $\text{MEM}(\text{TCNQ})_2$. As we shall see later, however, such a source of site inequivalence will always trigger the occurrence of an additional inequivalence involving vibronic distortion. The modified theory, which does not alter the qualita-

tive form of the excitation spectrum, is presented in this paper.

The experimentally measured excitation spectrum is found to be in complete accord with the theoretical spectrum. A definitive verification of the localized nature of the unpaired electron states in $\text{MEM}(\text{TCNQ})_2$ is thus established. A detailed fit of the theory to the experimental spectrum enables experimental values to be deduced for the physical constants that appear in the microscopic theory. These are (a) the intradimer π MO hopping or resonance integral t , (b) the TCNQ monomer a_g molecular vibration frequencies $\{\omega_\alpha\}$, (c) the TCNQ monomer a_g EMV coupling constants $\{g_\alpha\}$, and (d) the initial difference in energy $2\Delta_c$ of the inequivalent TCNQ monomer π MO's. The significance of the experimental values obtained for these quantities to the question of EMV coupling in TCNQ salts is discussed.

It is remarkable that the dimer charge oscillation which is specifically associated with the coupling of the unpaired electron to the high-frequency a_g CH-stretch mode ($\omega_1 = 3050 \text{ cm}^{-1}$) of the TCNQ molecule is observed in the present measurements. The value of the appropriate dimensionless EMV coupling constant involved here, $\lambda_\alpha \approx (g_\alpha^2/\omega_\alpha t)$, is of order 10^{-4} , which is two orders of magnitude smaller than typical values. That there should exist an extremely small, but nevertheless, finite electronic coupling to the CH stretch mode was predicted theoretically some years ago by Lipari and Duke.⁹ The experimental value we obtain for g_α is in excellent accord with their theoretical estimate of this quantity.

An interesting aspect of the one-electron state that accommodates the unpaired electron on the TCNQ dimer is that it involves *molecular distortion*. This is found to be a consequence of the *simultaneous* presence of the initial (steric) slight inequivalence of the monomer sites (Δ_c) and the monomer EMV coupling. In the absence of both of the latter factors the unpaired electron is shared equally among the two TCNQ monomers in a two-site bonding MO of energy $-t$, relative to the energy of the noninteracting TCNQ monomer π MO. With the introduction of Δ_c (alone) the familiar secular determinant is modified to

$$\begin{vmatrix} E - \Delta_c & t \\ t & E + \Delta_c \end{vmatrix} = 0$$

and the energy E of the bonding MO becomes $E = -(t^2 + \Delta_c^2)^{1/2}$, indicating an increased stability with respect to the former energy of $-t$. Now however, the unpaired electron is not shared

equally among the two monomer sites; its charge density is slightly greater at the monomer site with energy $-\Delta_c$ than at the site with energy Δ_c . But with the introduction of the monomer EMV coupling, an increase or decrease in charge density at a monomer site will lead to a lowering $-\Delta_v$, or raising Δ_v of the monomer π MO as the internal bond lengths readjust to the new local charge densities. The inequivalence of the monomer sites is therefore further enhanced, leading to an even more stabilized two-site bonding orbital. This process of increased stability is, however, counterbalanced by the elastic restoring forces associated with the internal molecular distortion. In the ensuing text of this paper it will be seen that the sum of the electronic and molecular distortion energies of the dimeric system is

$$E_D = -[t^2 + (\Delta_c + \Delta_v)^2]^{1/2} + \frac{1}{4} \sum_{\alpha} \omega_{\alpha} q_{\alpha}^2, \quad (1.1)$$

where $\Delta_c = \sum_{\alpha} (g_{\alpha}/\sqrt{2}) q_{\alpha}$ and $\{q_{\alpha}\}$ denote a set of distortion coordinates (defined explicitly in Sec. II). Minimization of (1.1) with respect to the latter determine the equilibrium values $\{q_{\alpha}^0\}$ of the distortion and hence of the additional distortion "gap" $\Delta_v^0 = \sum_{\alpha} (g_{\alpha}/\sqrt{2}) q_{\alpha}^0$. The energy of the two-site bonding MO is finally $E = -[t^2 + (\Delta_c + \Delta_v^0)^2]^{1/2}$. We shall refer to this electronic state as a "distorted dimer state."¹⁰ The steps of its evolution are illustrated schematically in Fig. 2. Examination of (1.1) reveals that there will *always* occur a non-vanishing distortion ($q_{\alpha}^0 \neq 0$) provided that Δ_c is finite ($\Delta_c \neq 0$). For vanishing Δ_c , no molecular distortion is possible—unless however, the quantity $E_p = \sum_{\alpha} (g_{\alpha}^2/\omega_{\alpha})$ exceeds the energy t . The initial inequivalence Δ_c plays, therefore a *catalytic* role in the formation of the distortion gap Δ_v^0 .

Our paper is organized as follows. In Sec. II we present the microscopic theory of the unpaired electron state and apply it to derive a theoretical formula for the frequency-dependent electrical conductivity of a system of N noninteracting ion-radical dimers. In Sec. III the procedure and results of our polarized-optical-reflectance measurements on MEM(TCNQ)₂ are presented. The

theoretical analysis of the experimental data is presented and discussed in Sec. IV. The main conclusions of the paper are summarized in a final section.

II. MICROSCOPIC THEORY OF THE DISTORTED DIMER

The microscopic model which we will employ to describe the one-electron states of the ion-radical dimer is defined by the following Hamiltonian ($\hbar = 1$):

$$H = H_e + H_v + \sum_{\alpha, i} g_{\alpha} n_i Q_{\alpha, i} - \vec{F} \cdot \vec{p}, \quad (2.1)$$

where

$$H_e = (E_0 + \Delta_c) n_1 + (E_0 - \Delta_c) n_2 + \sum_{\sigma} t (c_{2, \sigma}^{\dagger} c_{1, \sigma} + c_{1, \sigma}^{\dagger} c_{2, \sigma}), \quad (2.2)$$

$$H_v = \sum_{i, \alpha} \frac{1}{4} (\Pi_{\alpha, i}^2 + Q_{\alpha, i}^2) \omega_{\alpha}, \quad (2.3)$$

$$\vec{p} = \frac{1}{2} e \vec{a} (n_1 - n_2); \quad (2.4)$$

H_e is the Hamiltonian of the unpaired electron in the absence of vibronic coupling and consists of the interaction of the two monomer π MO's. $(E_0 + \Delta_c)$ denotes the energy of the (unperturbed) π MO of monomer 1, while $(E_0 - \Delta_c)$ denotes that for monomer 2. These energies are assumed to differ slightly ($\Delta_c \ll E_0$) on account of an asymmetric cation arrangement in the molecular crystal. E_0 is the common MO energy that would result in the absence of the asymmetric cation arrangement. $c_{i, \sigma}^{\dagger}$ and $c_{i, \sigma}$ denote site fermion creation and destruction operators for the unpaired electron, i labeling the monomer site ($i = 1, 2$) and σ the electronic spin. $n_i = \sum_{\sigma} c_{i, \sigma}^{\dagger} c_{i, \sigma}$ is the occupation number operator for the site i and t the π -MO hopping integral operating between the two monomer sites.

H_v is the Hamiltonian of the totally symmetric (a_g) internal modes of vibration of the monomers and the third term of (2.1) describes their (linear) coupling to the monomer π MO. $Q_{\alpha, i}$ denotes the (dimensionless) normal mode coordinate corresponding to the symmetric vibration α ($\alpha = 1, 2, \dots, G$) of the monomer i , while ω_{α} denotes its corresponding normal mode frequency. The set of G constants $\{g_{\alpha}\}$ denote the a_g monomer π -electron-molecular vibration (EMV) coupling constants.¹¹ In terms of the familiar vibrational creation ($a_{\alpha, i}^{\dagger}$) and destruction ($a_{\alpha, i}$) operators, we note that $Q_{\alpha, i} = a_{\alpha, i} + a_{\alpha, i}^{\dagger}$ and $\Pi_{\alpha, i} = a_{\alpha, i} - a_{\alpha, i}^{\dagger}$. For the TCNQ monomer, $G = 10$, and the magnitudes of the a_g frequencies span the wide range 140–3050 cm^{-1} .

The last term in (2.1) describes the interaction

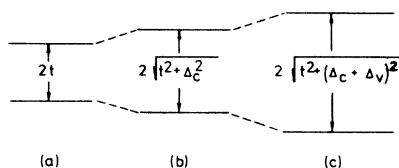


FIG. 2. Steps of evolution of the distorted dimer state; one-electron energy levels of the dimeric unit with (a) no site inequivalence, (b) steric-site inequivalence, and (c) steric-site inequivalence and vibronic coupling.

of the unpaired electron with an externally applied electric field \vec{F} . The operator \vec{p} , defined by Eq. (2.4), denotes the electric dipole moment of the dimer due to the presence of the unpaired electron. In Eq. (2.4) the vector length \vec{a} , whose magnitude will be of the order of the intermonomer separation, is specified in practice by the mode of the dimeric overlap.⁷ [In MEM(TCNQ)₂, for example, \vec{a} will be the intermonomer spacing in the direction of the crystal c axis].

The Hamiltonian (2.1) is similar to that studied by Rice⁷ for the ion-radical dimer with two unpaired electrons. In that study the site nonequivalence Δ_c was absent but it was necessary to allow for the on-site Coulomb repulsion U acting between the two unpaired electrons when occupying the same MO. For the present one-electron system the latter complication does not arise. Instead, we have the complication of Δ_c and to treat this problem it will be convenient to follow the analysis of Ref. 7.

We introduce the dimeric normal mode coordinates $q_\alpha = 2^{-1/2}(Q_{\alpha,1} - Q_{\alpha,2})$ and $s_\alpha = 2^{-1/2}(Q_{\alpha,1} + Q_{\alpha,2}) - s_\alpha^0$, with $s_\alpha^0 = -2^{1/2}g_\alpha/\omega_\alpha$ and the "charge-difference" operator $\delta n = n_1 - n_2$. Then noting that $N = n_1 + n_2$ is a constant of motion, equal to unity, the Hamiltonian (2.1) may be reexpressed as

$$H = H'_e + H_s + \sum_\alpha \frac{1}{4}(\pi_\alpha^2 + q_\alpha^2)\omega_\alpha + \sum_\alpha (g_\alpha/\sqrt{2})\delta n q_\alpha - \frac{1}{2}\vec{F} \cdot \vec{a} e \delta n, \quad (2.5)$$

where H'_e is given by Eq. (2.2) with the replacement $E_0 - E_0 - \frac{1}{2}E_p$, where $E_p = \sum_\alpha g_\alpha^2/\omega_\alpha$ is the conventionally defined "small-polaron" binding energy, and H_s is the harmonic Hamiltonian $H_s = \sum_\alpha \frac{1}{4}(\sigma_\alpha^2 + s_\alpha^2)\omega_\alpha$ for the symmetric normal modes s_α (σ_α and π_α denote the dimensionless canonical momenta coordinates conjugate to s_α and q_α , respectively). Equation (2.5) shows that the modes s_α are completely decoupled from the radical electron. They correspond to in-phase oscillations of the a_i modes of the two monomers and their frequencies are just ω_α . These frequencies may be measured in Raman-scattering experiments.

Now the equations of motion for the antisymmetric modes q_α are

$$\ddot{q}_\alpha + \omega_\alpha^2 q_\alpha = -2^{1/2}g_\alpha \omega_\alpha \delta n. \quad (2.6)$$

Because of the nonequivalence of the monomer sites, the Hamiltonian (2.5) indicates a ground-state average of δn , $\langle \delta n \rangle$, that is nonvanishing. According to (2.6) this will imply a nonvanishing equilibrium value

$$q_\alpha^0 = -2^{1/2}(g_\alpha/\omega_\alpha)\langle \delta n \rangle \quad (2.7)$$

for the modes q_α , i.e., the occurrence of internal molecular distortion. That this distortion leads to a further nonequivalence of the monomer sites may be seen by substituting the definitions $\delta q_\alpha = q_\alpha - q_\alpha^0$, $\delta \hat{n} = \delta n - \langle \delta n \rangle$ into the Hamiltonian (2.5). Ignoring the Hamiltonian H_s , (2.5) becomes

$$H = H_0 + H_{\text{int}}, \quad (2.8)$$

where

$$H_0 = (\Delta_c + \Delta_v)\delta n + V_{12} + \frac{1}{4} \sum_\alpha \omega_\alpha (q_\alpha^0)^2 + \frac{1}{4} \sum_\alpha \omega_\alpha (\delta \pi_\alpha^2 + \delta q_\alpha^2) - \vec{F} \cdot \vec{p}^0 + E_0 - \frac{1}{2}E_p \quad (2.9)$$

and

$$H_{\text{int}} = \left[\left(\sum_\alpha (g_\alpha/\sqrt{2})\delta q_\alpha \right) - \frac{1}{2}\vec{F} \cdot \vec{a} e \right] \delta \hat{n}. \quad (2.10)$$

In (2.9) V_{12} denotes the third term of (2.2),

$$\Delta_v = 2^{-1/2} \sum_\alpha g_\alpha q_\alpha^0 \quad (2.11)$$

and $\vec{p}^0 = \frac{1}{2}e\vec{a}\langle \delta n \rangle$. The term $-\vec{F} \cdot \vec{p}^0$ in H_0 is assumed to be cancelled by an equal and opposite energy arising from the asymmetric cations, i.e., the total equilibrium electric dipole moment of the crystalline unit cell is assumed to be zero. Equation (2.9) and (2.11) reveal that the site nonequivalence is increased from Δ_c to $\Delta = \Delta_c + \Delta_v$.

The electronic part of the Hamiltonian (2.9) leads to a ground-state (bonding) eigenfunction for the unpaired electron

$$|E_- \rangle = c_1 |\phi_1 \rangle + c_2 |\phi_2 \rangle, \quad (2.12)$$

with eigenvalue¹² $E_- = -(t^2 + \Delta^2)^{1/2}$, and to an excited-state (antibonding) eigenfunction

$$|E_+ \rangle = c_2 |\phi_1 \rangle - c_1 |\phi_2 \rangle, \quad (2.13)$$

with eigenvalue $E_+ = (t^2 + \Delta^2)^{1/2}$. In (2.13) and (2.14) $|\phi_i \rangle$ denotes the noninteracting π MO of the monomer i and the coefficients c_i are

$$c_1 = (1 + h^2)^{-1/2}, \quad c_2 = (1 + h_*^2)^{-1/2}, \quad (2.14)$$

in which

$$h_\pm = t/[\Delta \pm (\Delta^2 + t^2)^{1/2}]. \quad (2.15)$$

The Hamiltonian H_{int} , defined by Eq. (2.10), describes a weak coupling between the states $|E_- \rangle$ and $|E_+ \rangle$ resulting from the applied field \vec{F} and from the fluctuations δq_α in the antisymmetric vibrational coordinates q_α . This coupling will be treated in our subsequent derivation of the excitation spectrum of the dimer.

In order to calculate the equilibrium distortion values $\{q_\alpha^0\}$ and hence, the magnitude of Δ_v , Eq. (2.7) is to be evaluated with respect to the ground-state eigenfunction (2.12). This leads to the set

of simultaneous nonlinear equations

$$q_\alpha^0 = \sqrt{2} (g_\alpha / \omega_\alpha) [\Delta / (t^2 + \Delta^2)^{1/2}] \quad (\alpha = 1, 2, \dots, G). \quad (2.16)$$

These equations also follow from minimizing the ground-state average of H_0 with respect to q_α^0 [cf. Eq. (1.1) of the Introduction]. For the evaluation of the equilibrium value of Δ_v , Δ_v^0 , it is not necessary, however, to solve (2.16) for the individual values of q_α^0 , for if both sides of Eq. (2.16) are multiplied by $(g_\alpha / \sqrt{2})$ and then summed over α , we directly obtain the result

$$\Delta_v^0 = E_p(\Delta_c + \Delta_v^0) / [t^2 + (\Delta_c + \Delta_v^0)^2]^{1/2}, \quad (2.17)$$

or,

$$\Delta = \Delta_c + E_p \Delta / (t^2 + \Delta^2)^{1/2}, \quad (2.18)$$

for the required total gap $\Delta = \Delta_c + \Delta_v^0$. As discussed in Sec. I, the solution of (2.17) or (2.18) will always yield $\Delta > \Delta_c$, i.e., $\Delta_v^0 \neq 0$, provided $\Delta_c \neq 0$. If $\Delta_c = 0$, a nonvanishing solution for Δ_v^0 can arise only if $E_p > t$.

The Hamiltonian (2.9) describes $G + 1$ noninteracting elementary excitations. These are the electronic charge-transfer (CT) excitation, $|E_- \rangle \rightarrow |E_+ \rangle$, of frequency $\omega_{CT} = 2(t^2 + \Delta^2)^{1/2}$, and the set of G antisymmetric vibrations with frequencies $\{\omega_\alpha\}$. The first term of the Hamiltonian (2.10) shows that these excitations are linearly coupled to each other. If this term is compared with the second term of (2.10) it may be concluded that the fluctuations δq_α introduce the effective oscillating electric fields $\vec{F}_\alpha = (\sqrt{2} \tilde{a} / e a^2) g_\alpha \delta q_\alpha$. These fields will drive small amplitude oscillations in the charge difference δn and will also lead to a slight enhancement of the CT excitation frequency ω_{CT} . As discussed in Ref. 7 and elsewhere,⁸ the frequencies ω_α of the G "dimer charge oscillations" and the renormalized frequency Ω_{CT} of the CT excitation, may be shown, within the framework of linear response theory, to be given by the $G + 1$ solutions of the equation

$$\text{Re}[\tilde{\chi}(\omega)D(\omega)] = 1, \quad (2.19)$$

where $\tilde{\chi}(\omega) = \chi(\omega) / \chi(0)$;

$$\chi(\omega) = \langle E_+ | \delta \hat{n} | E_- \rangle^2 2\omega_{CT} / (\omega_{CT}^2 - \omega^2 - i\omega\gamma_e) \quad (2.20)$$

is the reduced CT electronic polarizability in the absence of vibronic coupling, and

$$\nu(\omega) = \sum_\alpha \lambda_\alpha \omega_\alpha^2 / (\omega_\alpha^2 - \omega^2 - i\omega\gamma_\alpha). \quad (2.21)$$

In (2.21), $\lambda_\alpha = E_p^\alpha \chi(0)$ characterizes the strengths of the individual CT excitation-molecular vibration couplings, where $E_p^\alpha = g_\alpha^2 / \omega_\alpha$. In (2.20) and

(2.21), γ_e and γ_α denote phenomenological natural widths of the originally uncoupled CT excitation and antisymmetric vibration mode α , respectively. The G dimer charge oscillations—which, essentially, are the modes δq_α renormalized—and the renormalized CT excitation Ω_{CT} , constitute the elementary excitations of the ion-radical dimer.

The frequency-dependent conductivity $\sigma(\omega)$ of a system of N such dimers, arbitrarily positioned and noninteracting with each other, has been derived to be⁷

$$\vec{\sigma}(\omega) = \sigma(\omega) \vec{A}, \quad (2.22)$$

$$\sigma(\omega) = -i\omega \frac{1}{4} e^2 a^2 (N/\Omega) \chi(\omega) / [1 - \tilde{\chi}(\omega)D(\omega)], \quad (2.23)$$

$$\vec{A} = N^{-1} \sum_j (\vec{a}_j \vec{a}_j / a^2). \quad (2.24)$$

In (2.23) Ω denotes the volume of the system and the quantity \vec{A} , in which the unit vector \vec{a}_j/a specifies the orientation of the dimer j ($j = 1, 2, \dots, N$), determines the tensorial character of $\vec{\sigma}(\omega)$. For a linear chain of dimers, such as occurs in MEM(TCNQ)₂, $\vec{A}_{\alpha\beta} = \delta_{\alpha c}^{K^r} \cdot \delta_{\beta c}^{K^r}$, where c denotes the chain axis and δ^{K^r} is the Kronecker delta. In this case $\vec{\sigma}(\omega)$ is polarized along the chain axis with magnitude $\sigma(\omega)$.

Expression (20) for $\chi(\omega)$ may be evaluated with the use of Eqs. (2.12), (2.13), and (2.14) to be

$$\chi(\omega) = (8t / \omega_{CT}) / (\omega_{CT}^2 - \omega^2 - i\omega\gamma_e). \quad (2.25)$$

Consequently, for the linear-chain system, it follows from (2.23) and (2.25) that the dielectric constant $\epsilon(\omega)$ along the c direction will be

$$\epsilon(\omega) = \epsilon_\infty + \frac{4\pi e^2 a^2 (N/\Omega) (2t^2 / \omega_{CT})}{\omega_{CT}^2 [1 - D(\omega)] - \omega^2 - i\omega\gamma_e}. \quad (2.26)$$

A constant dielectric constant ϵ_∞ , has been introduced to account for the effect of the remaining high-frequency electronic transitions of the molecular constituents of the crystal.

III. EXPERIMENTAL PROCEDURE AND RESULTS

Reflectance data at near normal incidence were obtained from MEM(TCNQ)₂ samples with well-shaped optical faces of approximate size $1 \times 5 \text{ mm}^2$. The chain direction (crystallographic c axis) was parallel to the long dimension of the samples.

Far-infrared data in the range $50\text{--}400 \text{ cm}^{-1}$ were taken with an RIIC FS720 Michelson interferometer equipped with a Cambridge Physical Sciences IGP220 polarizer. To obtain an acceptable signal-to-noise ratio in the far infrared, samples consisting of mosaics of aligned crystals were used. Absolute values were obtained by recording background spectra from sample mosaics covered with gold film. The spectral reso-

lution was $\sim 3 \text{ cm}^{-1}$

Measurements in the intermediate infrared (400–4000 cm^{-1}) were done on a single-beam reflectometer based on a Perkin Elmer (PE) 98 grating monochromator and with a PE gold grid polarizer mounted in front of the sample. Absolute values of reflectance were determined by covering part of the samples with an aluminum film and comparing the signals from the naked and covered parts. Corrections for the finite reflectance of aluminum have been made. The spectral resolution in the range of sharp molecular resonances was below 10 cm^{-1} . Several lines were scanned with higher resolution to ensure that the correct linewidths were obtained. The measurements were continued to 30 000 cm^{-1} using a PE98 quartz prism monochromator and a Nicol prism polarizer. In this high-frequency range, above all molecular vibration frequencies, the employed spectral resolution was fairly low: 200–500 cm^{-1} .

The overall accuracy in the absolute values of reflectance is estimated to be about 2%. The accuracy in the relative spectral dependence is somewhat better, perhaps about 1%.

In Fig. 3 we present the measured reflectance data. The frequency range is 50–30 000 cm^{-1} for R_{\parallel} (along the TCNQ stacks) and 50–16 000 cm^{-1} for R_{\perp} (perpendicular to the stacks).

R_{\parallel} shows a typical electronic absorption around 3500 cm^{-1} , no doubt associated with the radical electron-charge-transfer excitations along the

stacks. At higher frequencies a weak doublet appears around 10 000 cm^{-1} . The origin of this 10 000- cm^{-1} absorption is controversial,¹³ but it may arise from intramolecular absorption processes in the TCNQ molecule, since it is found at the same position in most TCNQ chain compounds.¹⁴ The weak structure at higher frequencies is definitely intramolecular in origin.

Below the charge-transfer band, extremely strong lines are seen in the range of molecular vibrations. An analysis of these lines and of the 3500- cm^{-1} absorption, based on the microscopic theory of Sec. II will be presented in the following section.

R_{\perp} in contrast is flat with a strength in the molecular lines typical for a molecular crystal. The overall level is 7–8%, as commonly found in TCNQ salts along the low-conductivity directions. The monitoring of R_{\perp} provides a direct check of polarizer efficiency. Note for example, that the very sharp drop in R_{\parallel} near 1350 cm^{-1} is not visible in R_{\perp} at all. Hence, the vibrational structure which coincides in R_{\perp} and R_{\parallel} can be fully trusted.

For use in the imminent theoretical analysis of the data, we have performed a dispersion analysis of R_{\parallel} to obtain the frequency-dependent conductivity $\sigma(\omega)$ (Fig. 4). The required extrapolations consisted of assuming R_{\parallel} constant and equal to 27% below 50 cm^{-1} , and 5.0% above 30 000 cm^{-1} . A change in extrapolation procedure will only give insignificant changes in $\sigma(\omega)$ in the range of principal interest. The extrapolation $R_{\parallel} = 27\%$

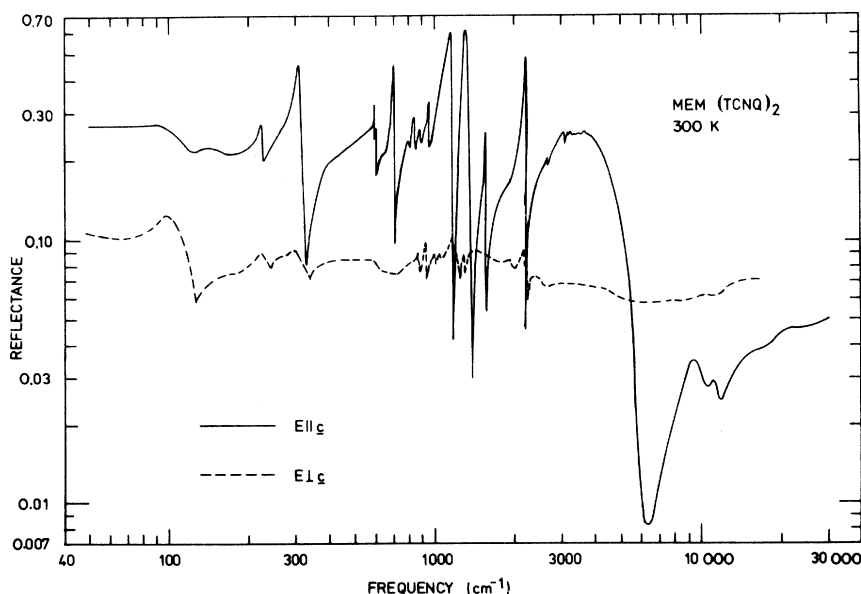


FIG. 3. The measured polarized optical reflectance of MEM(TCNQ)₂ at room temperature; full curve: electric field vector parallel to crystallographic c axis; broken curve: electric field vector perpendicular to c axis.

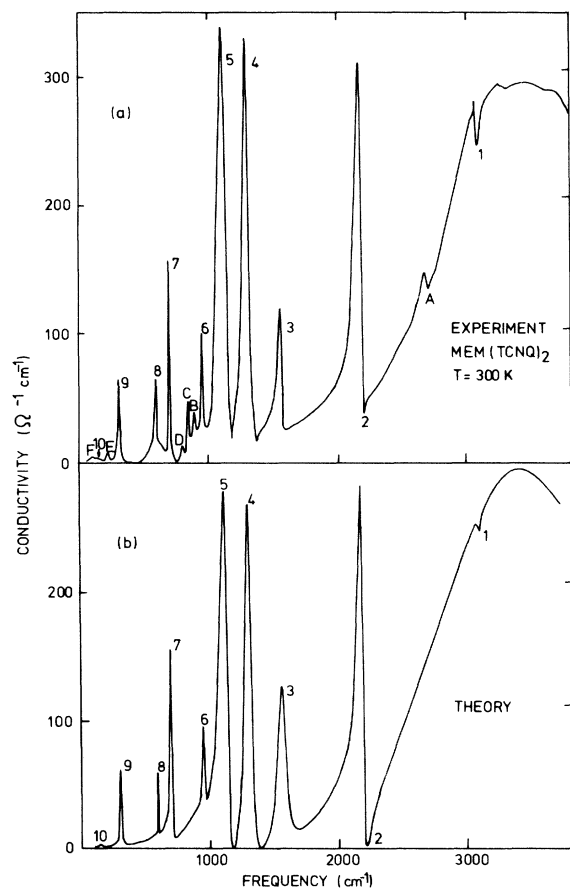


FIG. 4. Real part of the frequency-dependent conductivity along the crystallographic c axis, as deduced by dispersion analysis of the measured reflectivity (upper curve) and calculated on the basis of the microscopic theory of Sec. II.

below 50 cm^{-1} implies a static dielectric constant $\epsilon(0) = 10$ along the chain direction. This value of $\epsilon(0)$ is in agreement with microwave measurements undertaken by the Gröningen group.¹⁵

IV. ANALYSIS AND DISCUSSION

The experimentally determined real part of the frequency-dependent conductivity $\sigma(\omega)$ in the spectral range $50\text{--}3500 \text{ cm}^{-1}$, deduced from our measurement of R_{\parallel} , is shown in the upper portion of Fig. 4. The spectrum of elementary excitations revealed by $R(\sigma(\omega))$ is consistent with that expected for the ion-radical dimer. The broad electronic absorption centered about 3500 cm^{-1} may be interpreted as the primary electronic CT excitation band, implying $\Omega_{\text{CT}} \approx 3500 \text{ cm}^{-1}$. The molecular absorption features, labeled 1 through 10, may be interpreted as the ten dimer charge-oscillation bands. A theoretically calculated spectrum, provided by Eqs. (2.23) and (2.25), is shown in the lower portion of Fig. 4. It would appear to

confirm the dimer interpretation beyond reasonable doubt.

The latter theoretically calculated spectrum actually is a fit of Eqs. (2.23) and (2.25) to the experimental $R(\sigma(\omega))$ vs ω data. It was accomplished as follows. Three independent physical constants characterize a given absorption feature: its position along the ω axis, its (integrated) intensity, and its absolute height. Since we seek to fit a spectrum consisting of $G + 1$ absorption features, we are required to furnish a total of $3(G + 1)$ independent physical parameters. We chose these parameters to be $\{\omega_{\alpha}, \lambda_{\alpha}, \gamma_{\alpha}\}$ (for the G -dimer charge oscillations) and $\omega_{\text{CT}}, t^2/\omega_{\text{CT}}$, and γ_e (for the primary CT band). These parameters were varied so as to obtain an optimum fit of Eqs. (2.23) and (2.25) to the experimental data. The values, $a = 3.34 \text{ \AA}$ and $N/\Omega = 1.4 \times 10^{21} \text{ cm}^{-3}$, known from the crystal structure,² were employed in Eq. (2.23).

The optimum values found for the parameters were employed in Eq. (2.26) for $\epsilon(\omega)$ in order to calculate $R_{\parallel}(\omega)$. With the value $\epsilon_{\infty} = 1.8$ the cal-

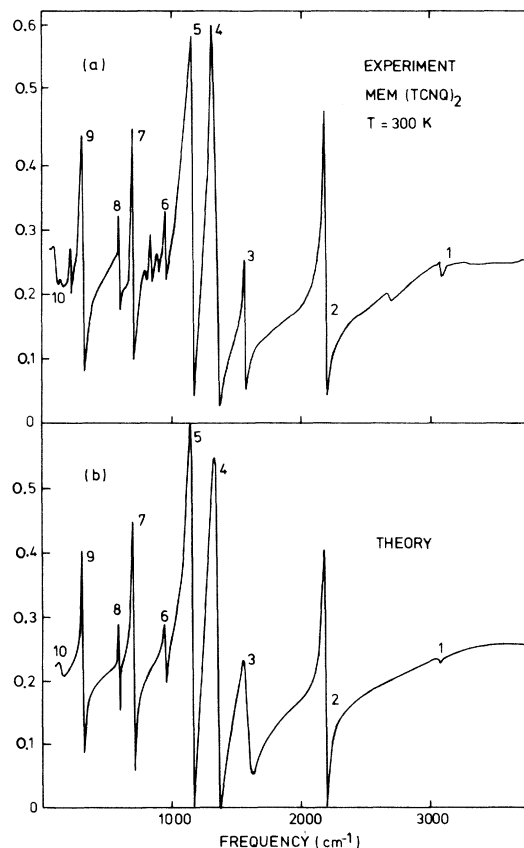


FIG. 5. Optical reflectance R_{\parallel} as measured (upper curve) and calculated on the basis of the microscopic theory of Sec. II (lower curve).

TABLE I. a_g vibrational modes of TCNQ (cm^{-1}).

Mode	Isolated molecule ^a		K-TCNQ ^b	MEM(TCNQ) ₂
	(TCNQ) ⁰	(TCNQ) ⁻		
1	3048			3070
2	2229	2206	2225	2210
3	1602	1615	1632	1630
4	1454	1391	1395	1395
5	1207	1196	1206	1180
6	948	978	848	958
7	711	725	723	718
8	602	613		597
9	334	337	333	324
10	144	148		150

^aAfter Girlando and Pecile, Ref. 16.^bAfter Rice, Lipari, and Strässler, Ref. 8.

culated reflectance is in remarkable agreement with the measured reflectance, as shown in Fig. 5.

The optimum values found for the parameters ω_{CT} , t^2/ω_{CT} and γ_e are $\omega_{CT} = 3250 \text{ cm}^{-1}$ (0.4 eV), $t^2/\omega_{CT} = 768 \text{ cm}^{-1}$, and $\gamma_e = 2000 \text{ cm}^{-1}$ (0.25 eV). The π -MO hopping integral is thus found to be $t = 1580 \text{ cm}^{-1}$ (0.195 eV). Also, since $\omega_{CT} = 2(t^2 + \Delta^2)^{1/2}$, we find the value of the total gap $\Delta = \Delta_c + \Delta_v^0$ to be $\Delta = 380 \text{ cm}^{-1}$ (0.05 eV). According to Eq. (2.18), Δ_c may be found from Δ provided E_p is known. We shall see that the experimental value we find for E_p is $E_p = 688 \text{ cm}^{-1}$ (0.085 eV). With this value for E_p , Eq. (2.18) yields $\Delta_c = 220 \text{ cm}^{-1}$ (0.03 eV). The distortion gap $\Delta_v^0 = \Delta - \Delta_c$ is thus $\Delta_v^0 = 160 \text{ cm}^{-1}$ (0.02 eV).

The values found for $\{\omega_\alpha\}$ and $\{\lambda_\alpha\}$ are listed in Tables I and II, respectively. In Table I the found set of values $\{\omega_\alpha\}$ are compared with those known for the isolated neutral¹⁶ and singly charged¹⁶ TCNQ molecule and those obtained⁸ for the TCNQ anion in the dimerized simple salt K-TCNQ. The values of the EMV coupling constants $\{g_\alpha\}$ may be derived from the relation

$$\lambda_\alpha = \chi(0)g_\alpha^2/\omega_\alpha = 8(t^2g_\alpha^2/\omega_{CT}^3\omega_\alpha), \quad (4.1)$$

where the second equality in (4.1) follows from Eq. (2.25). The resulting values for g_α are ex-

hibited in Table III in which, for comparison are included the theoretical values of g_α calculated by Lipari *et al.*⁹ Also included are experimental values of g_α previously obtained from optical-reflectance studies of¹⁷ TEA(TCNQ)₂ and⁸ K-TCNQ. From Tables I and III, the magnitude of $E_p = \sum_\alpha g_\alpha^2/\omega_\alpha$ for MEM(TCNQ)₂ is derived to be $E_p = 688 \text{ cm}^{-1}$ (0.085 eV).

Table III shows that the values $\{g_\alpha\}$ deduced from the present measurements compare favorably with the theoretical calculations of Lipari *et al.*⁹ Only for the two modes 8 and 6 do considerable differences arise. The small coupling constant g_{10} associated with the higher-frequency CH stretch mode is reported here for the first time and its value $g_{10} = 44 \text{ cm}^{-1}$ we consider to be in excellent accord with the theoretical estimate $g_{10} = 31 \text{ cm}^{-1}$ of Lipari *et al.* The present reported values of g_α also agree generally well with those previously deduced for¹⁷ TEA(TCNQ)₂ and⁸ K-TCNQ. The differences probably reflect the differences in the quality of the respective experimental data and hence the data's susceptibility to theoretical analysis. The charge oscillation driven by the CH stretch mode, the dimensionless coupling constant associated with which is only of the order of 10^{-4} , was neither observed in TEA(TCNQ)₂ nor K-TCNQ.

We note that several minor absorption features appear in the experimental spectrum which cannot be accounted for in terms of the expected dimer spectrum. In Fig. 4 these are labeled A through F. We believe the features C, E, and F arise from the IR active out-of-plane TCNQ modes (b_{3u}) which are known¹⁶ to occur at the frequencies 859, 220, and 103 cm^{-1} , respectively. At this time we cannot offer an explanation of the three remaining features A, B, and D. [The feature A, in the region of 2700 cm^{-1} , is also observed¹⁸ for TEA(TCNQ)₂, suggesting that it is associated with

TABLE II. Dimensionless EMV coupling constants λ_α .

$\omega_\alpha \text{ (cm}^{-1}\text{)}$	λ_α	$\omega_\alpha \text{ (cm}^{-1}\text{)}$	λ_α
3070	3.8×10^{-4}	958	0.004
2210	0.032	718	0.029
1630	0.104	597	2.5×10^{-3}
1395	0.104	324	0.058
1180	0.044	150	0.022

TABLE III. Electron-molecular-vibration coupling constants g_α (cm^{-1}).

Mode	Calculated ^a	K-TCNQ ^b	TEA(TCNQ) ₂ ^c	MEM(TCNQ) ₂
1	31			44
2	423	589	339	350
3	1057	670	524	540
4	392	573	419	500
5	229	331	323	300
6	237	339	194	85
7	263	169	177	190
8	18		105	50
9	194	177	234	180
10	78		153	75

^aAfter Lipari, Duke, Bozio, Girlando, and Pecile, Ref. 9.^bAfter Rice, Lipari, and Strässler, Ref. 8.^cAfter Rice, Pietronero, and Brüesch, Ref. 17.

the TCNQ stacks rather than the cations.]

If the values deduced above for Δ and t are substituted into Eqs. (2.14) and (2.15) the ground-state wave function (2.12) of the distorted dimer is found to be

$$|E_-\rangle = 0.62|\phi_1\rangle + 0.79|\phi_2\rangle. \quad (4.2)$$

Consequently, the mean charge residing on the monomer 1 is $q_1 = 0.38e$, while that residing on the monomer 2 is $q_2 = 0.62e$. A rudimentary independent estimate of q_1 and q_2 may be obtained from the known dependence on charge q of the length l of the bridging carbon double bond (C) of the TCNQ molecule [Fig. 6(a)]. The lengths of the C bond reported in Refs. 19–21 for the respective charge occupations of 0, 0.5, and 1.0 provides the plot q vs l drawn in Fig. 6(b). From the x-ray structure studies of MEM(TCNQ)₂, Bosch and van Bodegom² have determined $l = 1.386$ Å for monomer 1 and $l = 1.399$ for monomer 2. With these values of l , Fig. 6(b) yields the estimates

$q_1 = 0.26$ and $q_2 = 0.59$. The agreement with (4.2) is very reasonable in view of the obvious limitation inherent in the use of Fig. 6(b). For a more extensive discussion of the relation between the TCNQ internal bond lengths and the charge occupation we refer the reader to the paper by Flandrois and Chasseau.²²

V. CONCLUSIONS

This paper has investigated the nature of the unpaired electron states in the dimerized phase of the complex TCNQ salt MEM(TCNQ)₂. On the basis of polarized-optical-reflectance measurements and a theoretical analysis two basic conclusions have been arrived at. Firstly, each unpaired electron is localized on a dimeric TCNQ unit and occupies the two-site molecular orbital characteristic of the dimeric unit. The hopping integral t specifying the intradimer interaction of the two underlying monomer π MO's is experimentally found to be $t = 0.2$ eV. Secondly, the two-site molecular orbital involves molecular distortion which, interestingly, is driven by an initial (steric) site inequivalence of the individual TCNQ monomers. The energy of the bonding two-site MO relative to the energy of the noninteracting monomer π -MO energy is

$$E_- = -(E_p/2) - [t^2 + (\Delta_c + \Delta_v^0)^2]^{1/2},$$

where E_p denotes the conventionally defined small-polaron binding energy, Δ_c the initial nonequivalence of the monomer site energies, and Δ_v^0 the additional site nonequivalence due to molecular distortion. Experimentally, it is found that $E_p = 0.085$ eV, $\Delta_c = 0.027$, and $\Delta_v^0 = 0.02$ eV.

The localization of the unpaired electrons to the dimeric units is undoubtedly a consequence of the Coulomb repulsion between the unpaired electrons.

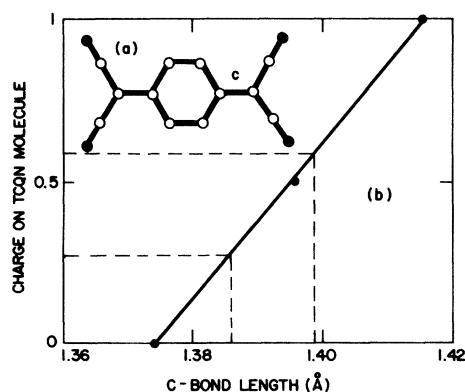


FIG. 6. Charge on TCNQ molecule as a function of the C-bond length (see text).

The latter suppresses the tendency to delocalization favored by the weak but finite interdimer interaction of the monomer π MO's. We note that the Gröningen workers³ have been able to explain the observed paramagnetism of MEM(TCNQ)₂ on the basis of the assumption that the dimerized TCNQ stack is equivalent to a half-filled Hubbard linear chain in which the atomic site is a TCNQ dimer and for which the on-site Coulomb repulsion U' greatly exceeds the intersite hopping integral t' . Such a model may be expected also to account for the observed dc transport properties.²³ The verification of the dimeric localization of the unpaired electrons in MEM(TCNQ)₂ established in this paper provides a firm basis for the use of the latter model for this complex TCNQ salt. We note that the model dictates the existence of quite different energy gaps for the excitations responsible for electrical conduction, spin paramagnetism, and optical absorption. The gap for electrical conduction is essentially U' , namely, the energy required to thermally promote a doubly

occupied and unoccupied dimer pair. For spin paramagnetism, the gap results from the weak interdimer antiferromagnetic exchange energy $4t'^2/U'$. The optical absorption gap, however, is the energy of the intradimer charge-transfer excitation Ω_{CT} .

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